

X-ray absorption of Si–C–N thin films: A comparison between crystalline and amorphous phases

Y. K. Chang, H. H. Hsieh, and W. F. Pong^{a)}

Department of Physics, Tamkang University, Tamsui 251, Taiwan, Republic of China

M.-H. Tsai

Department of Physics, National Sun Yat-Sen University, Kaohsiung 804, Taiwan, Republic of China

T. E. Dann,^{b)} F. Z. Chien, and P. K. Tseng

Department of Physics, Tamkang University, Tamsui 251, Taiwan, Republic of China

L. C. Chen and S. L. Wei

Center for Condensed Matter Sciences, National Taiwan University, Taipei 107, Taiwan, Republic of China

K. H. Chen and J.-J. Wu

Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 107, Taiwan, Republic of China

Y. F. Chen

Department of Physics, National Taiwan University, Taipei 107, Taiwan, Republic of China

(Received 4 May 1999; accepted for publication 17 August 1999)

X-ray absorption near edge structure (XANES) spectra of crystalline (*c*)- and amorphous (*a*)-Si–C–N thin films were measured at the C, N, and Si *K* edge using the fluorescence and sample drain current modes. A sharp peak similar to the C 1*s* core exciton in chemical vapor deposition diamond is observed, which can be assigned to the transition from the C 1*s* to *sp*³ hybridized states in *c*-Si–C–N. The C *K* edge XANES spectrum of *a*-Si–C–N contains a relatively large 1*s* → π^* peak, implying that carbon atoms in the *a*-Si–C–N film are bonded largely in graphite-like *sp*² configurations. A shift of the *a*-Si–C–N π^* peak towards the lower energy by ~ 0.3 eV relative to that of *c*-Si–C–N is observed, which can be attributed to a higher degree of disorder-induced localization of excited electrons. Both *a*- and *c*-Si–C–N N *K*-edge XANES spectra resemble that of α -Si₃N₄. The Si *K*-edge absorption spectra of the Si–C–N thin films indicate a proportional combination of local Si–N and Si–C bonds. The increase of the binding energies of excited electrons and the broadening of the spectral features by structural disorder are also observed in the Si *K*-edge XANES spectrum of the *a*-Si–C–N film. © 1999 American Institute of Physics. [S0021-8979(99)09422-0]

I. INTRODUCTION

Silicon carbide (Si–C) and silicon nitride (Si–N) have wide applications in mechanical, optical, and electronic devices.¹ Carbon nitride (C–N), a highly promising hard material, has also received increasing attention recently.^{2,3} In contrast, the ternary Si–C–N system has attracted lesser attention despite its potential technological importance. While performing Si *K*-edge extended x-ray absorption fine structure (EXAFS) studies of nanometric Si–C–N powders, Gheorghiu *et al.*⁴ and Tenegal *et al.*⁵ derived atomic structures that are somewhat controversial. Our recent C, N, and Si *K*-edge absorption measurements and first-principles calculations indicated that the crystalline (*c*)-Si–C–N thin film has a proportional combination of local Si–N and Si–C bonds indicative of a local tetrahedral C–Si–N₃ arrangement and a long-range ordered atomic structure around Si atoms.⁶

The presence of mixed coordinations around Si was also observed in the extended energy loss fine structure analysis at the Si *K* edge of the amorphous Si–C–N thin film.⁷ In this study, we analyze C, N, and Si *K*-edge x-ray absorption spectra of *c*- and *a*-Si–C–N thin films in order to elucidate the local electronic and atomic structures in the ternary Si–C–N system. A comparison is made between the spectra of the *c*- and *a*-Si–C–N thin films. Due to the absence of a long-range order in the amorphous phase, the excitonic binding energy is found to increase relative to that of the crystalline phase.^{8,9}

II. EXPERIMENT

The C, N, and Si *K*-edge x-ray absorption spectra of *c*- and *a*-Si–C–N films and the chemical vapor deposition (CVD)-grown diamond, polycrystalline α -Si₃N₄, β -SiC, and Si(100) films were measured using the high-energy spherical grating monochromator (HSGM) and InSb(111) double crystal monochromator (DCM) beamlines with an electron-beam energy of 1.5 GeV and a maximum stored current of 200 mA at the Synchrotron Radiation Research Center (SRRC), Hsin-

^{a)} Author to whom all correspondence should be addressed; electronic mail: pong@exafs.phys.tku.edu.tw

^{b)} Also at Synchrotron Radiation Research Center, Hsinchu, Taiwan 300, Republic of China.

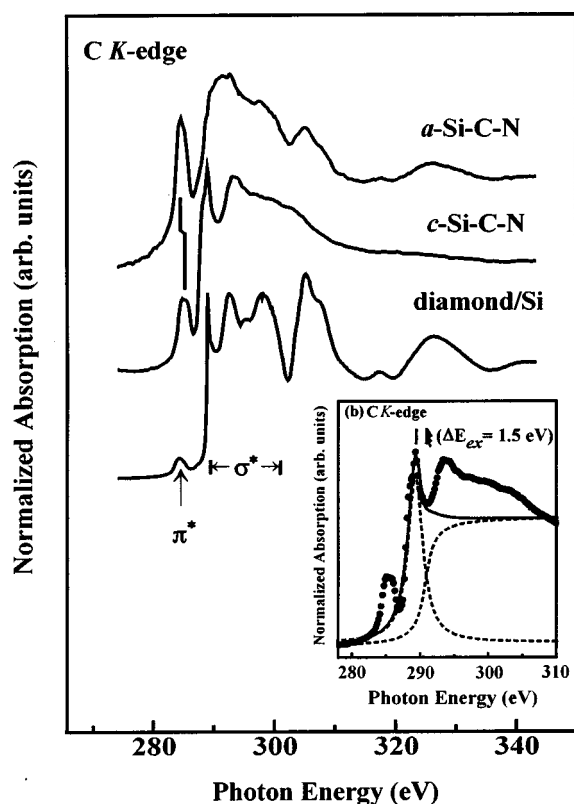


FIG. 1. Normalized C *K*-edge absorption spectra of *a*-Si-C-N, *c*-Si-C-N, and diamond/Si. The inset is in the vicinity of the C 1*s* core exciton resonance about 4 eV above the Fermi level of *c*-Si-C-N. The solid lines were calculated by a summation of the Lorentzian peak and the arctangent function shown by the dashed lines. The experimental data are shown by the filled circles.

chu, Taiwan. The spectra were measured using the fluorescence and sample drain current modes at room temperature. All fluorescence measurements for the N *K*-edge x-ray absorption near edge structure (XANES) spectra were performed using a seven-element Ge detector. Photon energies for C, N, and Si *K*-edge XANES measurements were calibrated using the bulk diamond,¹⁰ the well known CaF₂ thin film and the crystalline Si(100) film,¹¹ respectively. The typical resolution of the spectra was 0.2 eV for HSGM and 0.7 eV for DCM beamlines. In microwave plasma-enhanced chemical vapor depositions of *c*- and *a*-Si-C-N thin films, a mixture of H₂, CH₄, N₂, and SiH₄ gases was used as the source gases and the Si(100) wafer was used as the substrate. Details of the preparation procedure for similar compounds have been described elsewhere.¹² X-ray diffraction analyses reveal that the Si-C-N film prepared with a substrate temperature of ~840 °C contains polycrystallites, while the film prepared with a substrate temperature of ~600 °C has an amorphous phase. The scanning electron microscope (SEM) micrographs of Si-C-N are consistent with the x-ray results.

III. RESULTS AND DISCUSSION

In Fig. 1, we compare the C *K*-edge XANES spectra of *c*-Si-C-N, *a*-Si-C-N, and the CVD-grown diamond on the Si substrate (abbreviated hereafter as diamond/Si). After subtracting the pre-edge background, the spectra were nor-

malized using the incident beam intensity I_0 and were scaled to the maximum of the peak heights. For x-ray energies in the XANES region, the excited photoelectrons undergo a transition from the core state to unoccupied final states determined by the dipole-transition selection rule. The spectra shown in Fig. 1 reflect the transition from the C 1*s* core state to the *p*-like final states above the Fermi level. The spectrum of diamond/Si clearly shows sharp features similar to those reported in earlier literatures.^{10,13} The XANES for diamond has two features: (1) the spike of the C 1*s* core exciton resonance at approximately 289.2 eV and (2) a relatively broad σ^* feature of the sp^3 bonded carbon between about 290 and 302 eV. The relatively small peak at ~285 eV in the diamond/Si spectrum shown in Fig. 1, can be assigned to the graphite-like π^* states of sp^2 bonded carbon.^{14,15} The C *K*-edge XANES spectra of both *c*- and *a*-Si-C-N films are different from that of diamond/Si, which indicating that local environments of the carbon atom in both films are different from that of diamond. According to our previous theoretical calculations,⁶ the broad features in the energy range between ~293.5 and 302.4 eV in the C *K*-edge XANES spectra of the *c*-Si-C-N thin films can be attributed to transition to unoccupied C2*p*-derived states, which are hybridized with Si3*sp* and N2*sp* bands above the Fermi level. We find different fine structures in the spectra of *a*- and *c*-Si-C-N. The pre-edge π^* -like peak at 284.9 eV in the *a*-Si-C-N spectrum has a larger intensity and shifts slightly toward the lower energy by ~0.3 eV relative to that of *c*-Si-C-N. The relatively large $1s \rightarrow \pi^*$ peak suggests that carbon atoms in the *a*-Si-C-N film are bonded largely in the graphite-like sp^2 configuration indicative of a relatively large degree of disorder that increases the ratio of sp^2/sp^3 bonds, as shown in Fig. 1. It has been widely accepted that the lack of long-range order in the amorphous compound causes excited electrons to be more localized near the core hole due to the localized screening effect. This localization increases electron-hole interaction and, consequently, the binding energy of the excited electrons.^{8,9} Our finding of the binding energy shift of the excited electrons in the *a*-Si-C-N system agrees with earlier studies of carbon systems.¹⁵ On the other hand, a recent work on the structure of the nitrogen-doped tetrahedrally bonded amorphous carbon film indicated that the intensity of the $1s \rightarrow \pi^*$ feature increased with the N/C ratio, which was attributed to an excess N doping that promotes disordered sp^2 bonds.¹⁶ This is further supported by theoretical calculations for a wide range of stoichiometries in the amorphous carbon nitride system.¹⁷

The exciton state can be formed by the creation of a bound electron-hole pair with the absorption of a photon. The exciton energy level, E_{ex} , is slightly lower than the bottom of the conduction band (E_{CB}). The absorption spectra of semiconductors typically have a relatively sharp resonance superimposed with the threshold of the conduction band continuum.¹⁸ The excitonic binding energy, ΔE_{ex} , is given by $\Delta E_{ex} = |E_{ex} - E_{CB}|$, i.e., the energy separation between the exciton level and the conduction band edge. Herein, we use the Lorentzian and arctangent functions to describe the exciton resonance and the conduction band continuum,¹⁹ respectively. The inset of Fig. 1 (from Ref. 6)

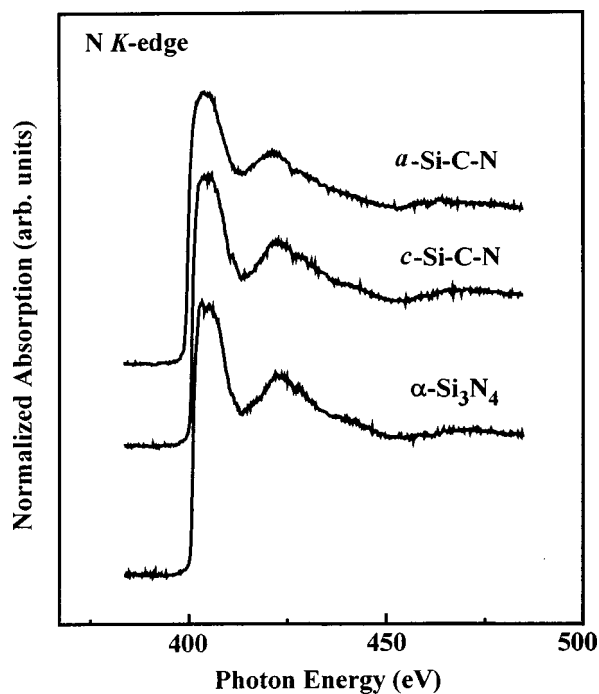


FIG. 2. Normalized fluorescence yield of the N *K*-edge absorption spectra of *a*-Si-C-N, *c*-Si-C-N, and α -Si₃N₄.

displays an enlargement of the part of the absorption data and the fitted spectrum for *c*-Si-C-N in the vicinity of the excitonic peak. According to the inset of Fig. 1, the excitonic peak is located at ~ 1.5 eV below the C 1*s* ionization energy (290.8 eV) at the inflection point of the continuous step. In contrast, the excitonic resonance peak essentially disappears in the spectrum of *a*-Si-C-N, which may be due to that the disorder-induced broadening of the resonance peak causes it to overlap strongly with the σ^* features and becomes unresolved. Another possibility is that the excitonic resonance is not supported in the amorphous phase because the lack of a long range order suppresses the hydrogen-like motion of the conduction electron around the core hole. Morar *et al.* indicated that the large dip at ~ 302.4 eV in the absorption spectrum of diamond/Si is a second absolute gap in the diamond band structure.¹⁰ The spectrum of *a*-Si-C-N also has a dip. However, it is although not as deep as that of diamond/Si. Thus, it cannot be interpreted as the existence of a second absolute gap.

Figure 2 displays the photon-flux-normalized N *K*-edge XANES spectra of *a*-Si-C-N, *c*-Si-C-N, and α -Si₃N₄. These three spectra are closely resemble each other except that the major peak at the threshold in the spectrum of *a*-Si-C-N appears to be composed of two features. Based on the calculated density of states of N 2*p* symmetry,⁶ the white line features in the N *K*-edge spectrum of *c*-Si-C-N can be attributed to the antibonding N 2*p*-Si 3*sp* and N 2*p*-C 2*sp* hybridized states. The similarity in the spectra of *a*-Si-C-N, *c*-Si-C-N, and α -Si₃N₄ suggests that, overall, nitrogen atoms have a similar local environment among those materials. Since α -Si₃N₄ contains only the N-Si bond, whereas *c*-Si-C-N/*a*-Si-C-N contains N-Si and C-Si bonds, the similarity in these spectra suggests that the sub-

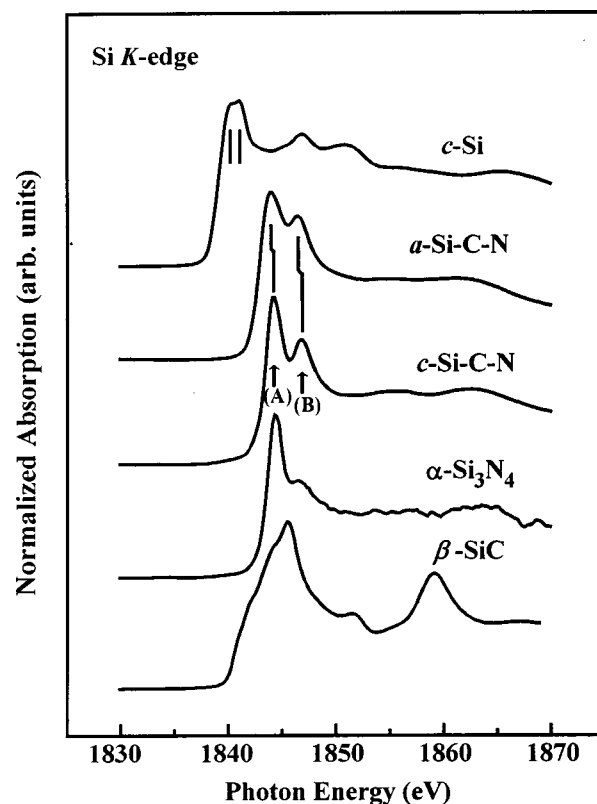


FIG. 3. Normalized Si *K*-edge XANES spectra of *c*-Si(100), *a*-Si-C-N, *c*-Si-C-N, α -Si₃N₄, and β -SiC.

stitution of N by C does not significantly alter the local bonding environment of N atoms.

Figure 3 displays the photon-flux-normalized Si *K*-edge XANES spectra of *c*-Si(100), *a*-Si-C-N, *c*-Si-C-N, α -Si₃N₄, and β -SiC. The Si *K*-edge XANES spectrum of *c*-Si(100) shows a transition from the Si 1*s* core state to the unoccupied Si 3*p*-derived states. This spectrum also contains characteristic double-peak features (labeled with two vertical solid lines) above the edge with an energy separation of about 1.0 eV. The threshold in the Si *K*-edge XANES spectra of *a*- and *c*-Si-C-N shift towards higher energies relative to that of *c*-Si(100) and the detailed shapes of the spectra differ distinctly from that of *c*-Si(100). These properties demonstrate that the chemical environment of the absorbing silicon atoms in *a*- and *c*-Si-C-N obviously differ from that of *c*-Si(100). Figure 3 also indicates that the Si *K*-edge XANES spectra of *a*-Si-C-N/*c*-Si-C-N and α -Si₃N₄ contain a primary peak (labeled A) and a shoulder (labeled B). However, in the *a*-Si-C-N/*c*-Si-C-N spectra, peak B is more prominent and peaks A and B appear to be well resolved. Peak B in the spectrum of *a*-Si-C-N/*c*-Si-C-N may be due to the local Si-C bonds around silicon atoms because the position of peak B relative to the threshold resembles that of the maximum peak of β -SiC. According to calculations,⁶ peaks A and B in the Si *K*-edge XANES spectrum of *c*-Si-C-N can be attributed to the antibonding Si 3*p*-N 2*sp* and Si 3*p*-C 2*sp* hybridized states. The Si 3*p*-N 2*p* and Si 3*p*-C 2*p* hybridized states contribute more significantly to the Si *K*-edge XANES spectra of Si-C-N. The calculated partial density of Si states agree with

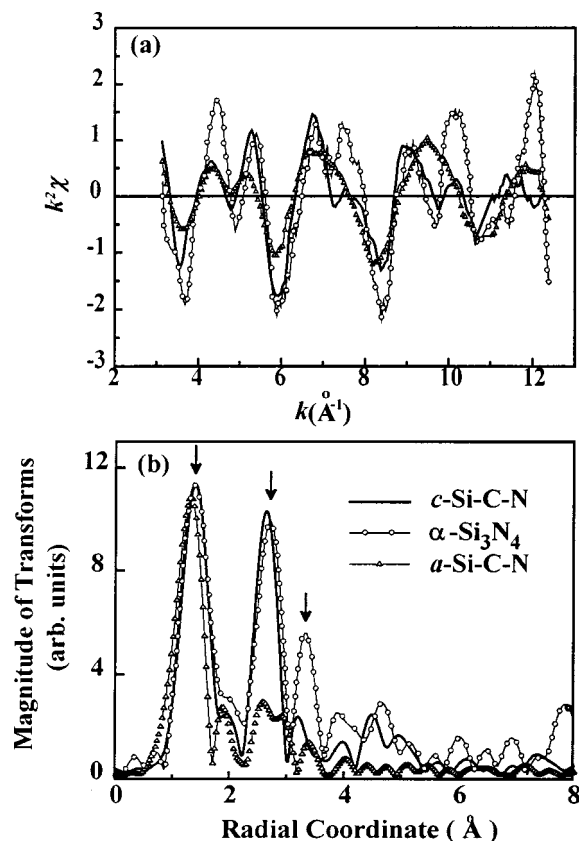


FIG. 4. (a) Normalized Si K -edge EXAFS oscillations $\chi(k)$ weighted by k^2 of a -Si-C-N (solid line with open triangles), c -Si-C-N (solid line), and α -Si₃N₄ (solid line with open circles) at room temperature. (b) Magnitude of Fourier transform of the EXAFS $k^3\chi$ data from $k=3.5$ to 12.0 \AA^{-1} . Structural parameters of the two NN obtained by fitting the Si K -edge EXAFS spectrum for a -Si-C-N/ c -Si-C-N: $N_{\text{Si-N}}=3 \pm 0.1/3 \pm 0.1$, $R_{\text{Si-N}}=1.72 \pm 0.01/1.73 \pm 0.01 \text{ \AA}$, $\sigma_{\text{Si-N}}^2=(7.9 \pm 0.5)/(3.8 \pm 0.5) \times 10^{-3} \text{ \AA}^2$. $N_{\text{Si-C}}=1 \pm 0.2/1 \pm 0.1$, $R_{\text{Si-C}}=1.87 \pm 0.01/1.88 \pm 0.01 \text{ \AA}$, $\sigma_{\text{Si-C}}^2=(6.9 \pm 0.5)/(3.6 \pm 0.5) \times 10^{-3} \text{ \AA}^2$. N , R , and σ^2 are the coordination number, NN distance, and mean-square vibrational amplitude, respectively.

the Si K -edge data and are also consistent with those of C and N K -edge XANES data, thereby confirming the occurrence of local Si-N and Si-C bonds in c -Si-C-N. Peak A (located at 1844.2 eV) and peak B (located at 1846.8 eV) in the c -Si-C-N spectra are well resolved. In the spectrum of a -Si-C-N, peak A (located at 1843.9 eV) is broader and peak A and peak B (located at 1846.5 eV) are less resolved. The increase of the binding energy of excited electrons and the structural-disorder induced broadening of the spectral peaks were also observed in the Si $L_{2,3}$ -edge XANES spectra of amorphous Si-based semiconductors.⁸

To determine the local structure around the silicon atoms and to support the conclusions made from the Si K -edge XANES data, EXAFS measurements were also performed at the Si K edge for the Si-C-N films used in this study. The normalized EXAFS oscillation $\chi(k)$ weighted by k^2 for the Si K edge and the corresponding Fourier transforms (FT) of the $k^3\chi$ data are shown in Fig. 4. According to Fig. 4(b), the position of the first main peak for a -Si-C-N, which corresponds to the nearest-neighbor (NN) Si-N and Si-C bond lengths (labeled by the first vertical arrow), is shifted slightly toward the lower R by $\sim 0.01 \text{ \AA}$ relative to that of

c -Si-C-N. The slight contraction of the nearest-neighbor distance reflects an increased importance of nearest-neighbor bonding in disordered or amorphous phase. The amorphous phase lacks the long-range order and the corresponding merit of the lowering of the electronic energy by the extended periodic potential. The short-ranged couplings among neighboring atoms become the dominant contribution to the cohesive energy of this material. The height of the first peak for a -Si-C-N in Fig. 4(b) is only slightly lower than that for c -Si-C-N, which indicates that the coordination numbers of the Si atoms in a -Si-C-N is approximately the same as that in c -Si-C-N. The similarity in the first peak also reveals that the local atomic structure of a - and c -Si-C-N closely resemble that of α -Si₃N₄, which indicates the existence of a predominantly α -Si₃N₄ network in the Si-C-N films.⁶ Figure 4(b) also reveals that a -Si-C-N has a Debye-Waller factor roughly two times larger than that of c -Si-C-N. The second peak near 2.8 \AA in Fig. 4(b) corresponds to the multiple next-nearest-neighbor (NNN) bond lengths (labeled by the second vertical arrow). The heights of the split NNN peaks for a -Si-C-N are also greatly reduced relative to that of c -Si-C-N by a factor of about 4. The split third-nearest-neighbor peaks for a -Si-C-N are also greatly reduced relative to that of c -Si-C-N (labeled by the third vertical arrow). These EXAFS results confirm our previous arguments of a greater disorder and/or decreased correlation of longer-distance shells in the amorphous phase. Combining both Si K -edge XANES and EXAFS results for a - and c -Si-C-N thin films, it can be concluded that most Si atoms prefer a local structure similar to that of α -Si₃N₄ with a local C-Si-N₃-like tetrahedral arrangement around the Si atoms.

IV. CONCLUSION

Results of our C K -edge XANES measurements indicate that the shift of the π^* peak toward lower energy by $\sim 0.3 \text{ eV}$ from c -Si-C-N to a -Si-C-N can be interpreted as a higher degree of disorder-induced localization of the excited electrons. The C K -edge XANES spectrum of a -Si-C-N is found to contain a relatively large $1s \rightarrow \pi^*$ peak, suggesting that carbon atoms in the a -Si-C-N film are bound largely in graphite-like sp^2 configuration. The nearly identical features in the N K -edge XANES spectra of a -Si-C-N/ c -Si-C-N and α -Si₃N₄ indicates that a -Si-C-N/ c -Si-C-N and α -Si₃N₄ have a similar local environment around the nitrogen atoms. The Si K -edge XANES and EXAFS measurements confirm the existence of a local tetrahedral C-Si-N₃ arrangement in the Si-C-N thin films. Due to a larger Debye-Waller factor, the magnitude of the second main peak in the FT curve of the a -Si-C-N reduces more significantly than of c -Si-C-N.

ACKNOWLEDGMENTS

One of the authors (W. F. P.) would like to thank the National Science Council of R.O.C., for financially supporting this research under Contract No. NSC88-2112-M-032-009. SRRC is appreciated for the use of their HSGM and DCM beamlines.

- ¹M. Dayan, J. Vac. Sci. Technol. A **3**, 361 (1985); E. C. Paloura, J. Lagowski, and H. C. Gatos, J. Appl. Phys. **69**, 3995 (1991), and references therein.
- ²M. L. Cohen, Phys. Rev. B **32**, 7988 (1985).
- ³A. Y. Liu and M. L. Cohen, Science **245**, 841 (1989).
- ⁴A. Gheorghiu, C. Senemaud, H. Roulet, G. Dufour, T. Moreno, S. Bodeur, C. Reynaud, M. Cauchetier, and M. Luce, J. Appl. Phys. **71**, 4118 (1992).
- ⁵F. Tenegal, A. M. Flank, and N. Herlin, Phys. Rev. B **54**, 12029 (1996).
- ⁶Y. K. Chang, H. H. Hsieh, W. F. Pong, M.-H. Tsai, K. H. Lee, T. E. Dann, F. Z. Chien, P. K. Tseng, K. L. Tsang, W. K. Su, L. C. Chen, S. L. Wei, K. H. Chen, D. M. Bhusari, and Y. F. Chen, Phys. Rev. B **58**, 9018 (1998).
- ⁷A. Bendeddouche, R. Berjoan, E. Beche, T. Merle-Mejean, S. Schamm, V. Serin, G. Taillades, A. Pradel, and R. Hillel, J. Appl. Phys. **81**, 6147 (1997).
- ⁸F. Evangelisti, F. Patella, R. A. Riedel, G. Margaritondo, P. Fiorini, P. Perfetti, and C. Quaresima, Phys. Rev. Lett. **53**, 2504 (1984).
- ⁹A. Gutierrez and M. F. Lez, Europhys. Lett. **31**, 299 (1995).
- ¹⁰J. F. Morar, F. J. Himpsel, G. Hollinger, G. Hughes, and J. L. Jordan, Phys. Rev. Lett. **54**, 1960 (1985).
- ¹¹W. F. Pong, Y. K. Chang, R. A. Mayanovic, G. H. Ho, H. J. Lin, S. H. Ko, P. K. Tseng, C. T. Chen, A. Hiraya, and M. Watanabe, Phys. Rev. B **53**, 16510 (1996).
- ¹²L. C. Chen, C. Y. Yang, D. M. Bhusari, K. H. Chen, M. C. Lin, J. C. Lin, and T. J. Chuang, Diamond Relat. Mater. **5**, 514 (1996).
- ¹³Y. Ma, N. Wassdahl, P. Skytt, J. Guo, J. Nordgren, P. D. Johnson, J. E. Rubensson, T. Boske, W. Eberhardt, and S. D. Kevan, Phys. Rev. Lett. **69**, 2598 (1992).
- ¹⁴J. Nithianandam, J. C. Rife, and H. Windischmann, Appl. Phys. Lett. **60**, 135 (1992).
- ¹⁵A. Gutierrez, M. F. Lopez, I. Garcia, and A. Vazquez, J. Vac. Sci. Technol. A **15**, 294 (1997).
- ¹⁶V. S. Veerasamy, J. Yuan, G. A. J. Amaratunga, W. I. Milne, K. W. R. Gilkes, W. Weiler, and L. M. Brown, Phys. Rev. B **48**, 17954 (1993).
- ¹⁷F. Weich, J. Widany, and Th. Frauenheim, Phys. Rev. Lett. **78**, 3326 (1997).
- ¹⁸C. Kittel, *Introduction to Solid States Physics*, 6th ed. (Wiley, New York, 1986).
- ¹⁹J. Stöhr, *NEXAFS Spectroscopy* (Springer, Berlin, 1992).